

Thermoviscoelastic Properties of Phenolic Resin/Polymeric Isocyanate Binders System¹

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ABSTRACT

Thermoviscoelastic properties of phenolic resin/polymeric isocyanate binders system are reported in this paper. The effects of blend composition and the reaction between the binders on these properties of the system are also considered. The viscous properties of binders and their blends were measured using computer controlled rotational viscometers (Brookfield HBDV-II+ and HAAKE "Rotovisco 12" rheometer in a cone and plate mode). The elastic properties of the phenolic urethane polymer (the blend composition) were measured by means of modified jet thrust technique based on measuring the thrust of a jet of liquid.

We determined that although both binders are Newtonian liquids, their blends exhibit viscoelastic non-Newtonian fluid flow behavior. The fluidity of the blends decreases both with time and with an increasing Part I content, and may reach comparatively large values at large values of either parameter. This behavior is explained as a result of the rubbery nature of the phenolic urethane polymer, which was produced as a product of reaction between Parts I and II. Using the jet thrust method allowed determination of the relaxation time of various blends at different values of shear rate.

KEY WORDS: thermoviscoelastic properties; viscosity; elasticity; relaxation time; polymer.

1. INTRODUCTION

Coldbox process was introduced to the foundry industry at 1968. It allowed to produce cores with good tensile strength, hot strength and high dimensional accuracy. The phenolic urethane amine coldbox process is the most prevalent one in the metal casting industry. The relatively low cost and general availability of binders for this process, along with their many versatile properties, have created a broad market for these materials. Moreover, this process can be used with all types of sands available. The process uses a two-part binder system, including a Part I binder (a phenol formaldehyde polymer blended with solvents and additives), and a Part II binder (a polymeric methylenebis-phenol diisocyanate). Sand is coated with the Part I and Part II components and blown into a pattern at room temperature. The tertiary amine catalyst vapor then purged through the pattern to harden the contained sand-binders mixture instantly. This cycle is followed by an air purge to introduce amine vapor throughout the sand mass and to remove residual amine from the hardened core [1].

A phenol formaldehyde polymer and a polymeric methylenebis-phenol diisocyanate are blended with solvents to yield low viscous resin solutions to facilitate their blending and coating the sand. The hydroxyl groups of the phenolic resin react with the isocyanate groups of the polymeric isocyanate. In the presence of the amine catalyst this reaction produces the solid urethane resin. This urethane resin bonds the sand grains together.

The developments about binders have concentrated on improving several drawbacks of their properties. Most binders require the following property improvements:

- the speed of the reaction between Part I and Part II must be controllable;
- phenolic urethane polymer structure must have enough hot strength for use in all types of metal castings;
- resin coated sand must have high flowability until the desired strip time.

Investigations about the binders have been done due to their commercial importance. For example, the compressive strength of system has widely been encountered in previous works [2]. However, there are few data about rheological properties of Part I and Part II, and no data of their blends.

These binders and their blends in foundry processes frequently require rheological characterization for flow equipment design. To set up a more or less complicated mathematical models (analytical or numerical) of a sand-binders mixing and a sand coremaking process requires more information about rheological and thermal properties of binders and their blends. The problem of the experimental rheologist is the engineering approach that is to say, the development of quantitative design procedures based on the measured properties of real material.

In this article, the thermoviscoelastic properties of binders (Parts I and II) are reported. The effects of blend composition and the reaction between the binders on the rheological and thermal properties of system are also considered.

TEST MATERIALS, EXPERIMENTAL APPARATUS AND PROCEDURE

As a coldbox binder system we used ISOCURE system produced by Ashland Chemical Company, Dublin, OH. This system consists of an ISOCURE Part I phenol-

formaldehyde binder and an ISOCURE Part II binder containing a polymeric isocyanate with solvents and additives.

ISOCURE Part I binder is a clear, amber liquid with density 1.12 g/cm^3 . ISOCURE Part II binder is a dark brown liquid with density 1.13 g/cm^3 . The reaction between Part I and Part II results in the formation of phenolic urethane polymer.

According to the existing procedure of sand coremaking process in foundry industry and following the manufacturer's instructions, in most experiments we used the blend composition at a 55/45 ratio of ISOCURE Part I binder to ISOCURE Part II binder components. To calibrate the experimental apparatus we used Glycerol/water mixtures as Newtonian liquid, and polyacrylamide solutions as non-Newtonian viscoelastic liquid.

The viscous properties of binders and their blends were measured using computer controlled rotational viscometers:

- (i) Brookfield HBDV-II+ viscometer. Disc and cylindrical spindles were used as sensors. Angular velocities of spindles were from 0 to 100 rpm.
- (ii) HAAKE "Rotovisco 12" rheometer in a cone and plate mode. Cone geometry has 0.00872 radian in angle and 2.5 cm in radius. The rotation speed of the cone was from 0 to 512 rpm. The thermal analyses were performed at temperature range from 20 to 60° C .

Both Brookfield HBDV-II+ and HAAKE "Rotovisco 12" rheometers were calibrated by using Newtonian and non-Newtonian calibration liquids. The calibration data for the dynamic viscosity as a function of temperature and shear rate were in good agreement with data from literature [3].

The elastic properties of the phenolic urethane polymer (the blend composition) were measured by means of a jet thrust technique. This method based on measuring the thrust of a jet of liquid. The average axial stress in the liquid at the nozzle exit is the difference between the momentum flux and measured thrust (corrected for surface tension effects) divided by the cross sectional area of the jet [4]. For developed velocity profiles in tubes the momentum flux is determined as [5]

$$T_{d.v.p.} = 1.33 T_{f.t.} , \quad (1)$$

where $T_{f.t.}$ is a momentum flux for a jet with a flat-topped velocity profile and the same density and viscosity as the liquid under the test.

The average axial stress in the liquid at the tube exit is [6],

$$\tau_{11} = 4(T_N - T_m) / \pi D^2 , \quad (2)$$

where T_m is the measured thrust, T_N is the thrust of a jet of Newtonian liquid of similar density and viscosity, D is the diameter of the tube.

The measured thrust should be corrected for surface tension effects [7]

$$T = T_m + \pi D \sigma , \quad (3)$$

where σ is the surface tension.

Oliver and Ashton [5] suggested to plot the data non-dimensionally as $(T/T_{f.t.} - 1)\rho/\rho_w$ versus the Reynolds number, where ρ and ρ_w are the densities of test liquid and water, respectively. The data for Newtonian (inelastic) and elastic liquids should be plotted in this way. The dimensionless separation of the two lines multiplied by $\rho_w \langle v \rangle^2$ gives the average axial stress τ_{11} , where $\langle v \rangle$ is the average exit velocity of the test liquid. The axial stress in liquid at tube exit τ_{11} may be plotted against the flow shear rate in tube.

The Figure 1 illustrates a modified equipment used for the axial stress measurements. A test liquid by compressed air from a stainless steel cylinder (1) was provided into a stainless steel capillary tube (3). This tube had a length 220 mm and an internal diameter of 1.5875 mm. A horizontal jet of test liquid strikes the light aluminum disk (9) connected to load cell (5) and then drains into beaker (6). The pressure on the entrance to the capillary tube was measured by a pressure gauge (4). Using water bath (2) controlled the temperature of the test liquid. The outputs of the load cell (5) and the pressure gauge (4) are fed to computer (7). The load cell was calibrated in a vertical position, with the aluminum disk upward, by placing weights in its center.

RESULTS AND DISCUSSION

Figure 2 shows the dynamic viscosity of binders ISOCURE Part I and ISOCURE Part II as a function of angular velocity of spindle at $t=23^{\circ}\text{C}$. It is obvious that the dynamic viscosity of Part I and Part II is not affected by shear rate (or angular velocities of spindle). Therefore both liquids may be adequately described by Newtonian fluid model. In our experiments we determined that the dynamic viscosity (or shear stress) of ISOCURE Part II shows nearly no temperature dependence from 20 to 60°C . In contrast, the dynamic viscosity (or shear stress) of ISOCURE Part I decreases with increasing temperature (Figure 3). At relatively low shear rates the shear stress decreases slowly with increasing temperature and at $\sim 60^{\circ}\text{C}$ it approaches that of steady dynamic viscosity.

Figure 4 shows the dynamic viscosity of the Part I/Part II blend as a function of ISOCURE Part I composition for different time intervals at fixed spindle angular velocity

($\omega = 50$ RPM) and temperature ($T = 23^0$ C). As seen from this figure, the viscosity increases with the ISOCURE Part I content. The increasing in dynamic viscosity of blends should be expected as the result of a rubbery nature of the phenolic urethane polymer which was produced in reaction between Parts I and II. Therefore, the viscosity of the blend also increases with time. For example, for Part I / Part II blend in ratio 55/45 (concentration recommended by manufacturer based on the sand cores qualities) the viscosity after 15 minutes increases almost three times.

The dynamic viscosity of Part I / Part II mixture in ratio 55/45 at different spindle angular velocities and temperatures is represented in Figure 5. It is obvious that the mixture exhibits a shear thinning non-Newtonian fluid flow behavior. However, the viscosity of mixture is restored with decreasing the spindle angular velocity. Therefore, one would suggest that as the spindle angular velocity is increased, the polymer chains of the urethane resin structure is oriented in the direction of flow and is disentangled from one another, hence, its dynamic viscosity decreases (Fried, 1995). At high angular velocities of spindle (>80 rpm) the behavior of liquid may slightly different from Newtonian.

To quantify non-Newtonian flow, we introduced the “thixotropic index” which is the ratio of the fluid’s viscosity as measured at two different speeds. The viscosity value at the lower speed (η_l) should be placed in the numerator, the one at the higher speed (η_h) in the denominator. Thixotropic index is defined by following expression:

$$\Gamma = -\log \left(\frac{\eta_l}{\eta_h} \right). \quad (4)$$

Figure 6 represents the variation of the “thixotropic index” with spindle angular velocity for Part I / Part II blend in ratio 55/45. As seen from this figure, as the degree of pseudoplastic behavior increases, the “thixotropic index” exceeds “1”.

Due to continuous temperature measurements during viscometric tests we observed a temperature rise in mixture of binders. We present in Figure 7 the temperature change of the ISOCURE Part I / ISOCURE Part II mixture (in ratio 55/45) in time as measured by computer operated thermocouple. At first 40 seconds the temperature increases dramatically from 23 to 30.7⁰ C. Further, the temperature of mixture decreases until to reach the initial temperature. One is drawn to the inescapable conclusion that the mixing of ISOCURE Part I and ISOCURE Part II binders yields thermoreaction. It is of practical interest to observe the variation of the viscosity of Part I / Part II blend with the time. At constant spindle angular velocities due to structural changes (Figure 8) the dynamic viscosity of ISOCURE Part I / ISOCURE Part II mixture increases rapidly. Due to the combined effects of the thermoreaction and structural phenomena, after ~ 50 min the viscosity does not change noticeably during 10-15 min. Then, viscosity continues to increase, and after 250 min the viscosity reaches a limit and becomes essentially time-independent. Here one would conclude that at this point the crosslinking process is over and the material reaches its shear-independent viscosity.

The first normal stress difference

$$N = \tau_{11} - \tau_{22} \quad (5)$$

for the ISOCURE I / ISOCURE II mixture in ratio 55/45 is measured by the jet thrust method described above, and the relaxation time λ is computed from,

$$\lambda = \frac{(\tau_{11} - \tau_{22})}{2 \dot{\gamma} \tau} = \frac{N}{2 \dot{\gamma} \tau}, \quad (6)$$

and the results are plotted in Figures 9 and 10.

From the same data plotted as a fluidity coefficient (reverse value of dynamic viscosity) versus spindle angular velocity (Figure 11) it may be concluded that the mixture of binders can be described by the “generalized linear fluidity model” introduced by Kutateladze et al. (1966),

$$\varphi = \varphi_0 + \theta_T T, \quad (7)$$

where $T = \tau + (\tau_{11} - \tau_{22})$; φ_0 is the fluidity in the limit of $T \rightarrow 0$; and θ_T is the structural fluidity coefficient. Experimental data show that Part I / Part II blend in ratio 55/45 is characterized by following values of these coefficients:

$$\varphi_0 = 0.0032 \text{ mPa}^{-1} \text{ s}^{-1}; \theta_T = 0.0001 \text{ Pa}^{-2} \text{ s}^{-1}.$$

CONCLUSIONS

The rheological and thermal properties of a phenolic resin (ISOCURE Part I) and polymeric isocyanate (ISOCURE Part II), and their blends are investigated experimentally. We determined that although both binders are Newtonian liquids, their blends exhibit non-Newtonian shear thinning fluid flow behavior and elasticity. The viscosity of the blends increases both with time and with increasing the ISOCURE Part I content, and may reach comparatively large values at large values of either parameter. The increasing in viscosity of blends is explained as the result of a rubbery nature of the phenolic urethane polymer,

which was produced as a product of reaction between Parts I and II. Due to the polymer chains being oriented in the direction of flow and disentangling from one another at high shear rates the viscosity of blend decreases. At fixed shear rates we observed a temperature rise during the mixing of binders. Using a jet thrust method the normal stresses and the relaxation time of blends were determined at different values of shear rate and temperature. The experimental data revealed that the “generalized linear fluidity model” could adequately describe the mixture of binders.

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FIGURE CAPTIONS

Fig. 1. Modified jet thrust apparatus: 1 – stainless steel cylinder filled by test liquid; 2 – water bath; 3 – capillary tube; 4 – pressure gauge; 5 – load cell; 6 – beaker; 7 – computer; 8 – manometer; 9 – light aluminum disk.

Fig. 2. Viscosity measurements for ISOCURE Part I and ISOCURE Part II at $T=23^0$ C.

Fig. 3. Variation of viscosity of Part I and Part II against temperature ($\omega = 50$ RPM).

Fig. 4. Variation of viscosity of Part I and Part II blend as a function of Part I composition at different time intervals ($\omega = 50$ RPM, $T = 23^0$ C).

Fig. 5. Variation of Part I / Part II blend (55/45) against spindle angular velocity ($T = 23^0$ C).

Fig. 6. Variation of Thixotropic index with spindle angular velocity for Part I / Part II blend in 55/45 ratio at $T=23$ C.

Fig. 7. Variation of temperature yielded at thermoreaction between Part I / Part II in ratio 55/45 against time.

Fig. 8. Variation of viscosity of Part I / Part II blend in ratio 55/45 against time at $\omega = 50$ RPM.

Fig. 9. Variation of first normal stress difference of Part I / Part II blend in ratio 55/45 against shear rate.

Fig. 10. Variation of relaxation time of Part I / Part II blend in ratio 55/45 against shear rate.

Fig. 11. Variation of fluidity coefficient of Part I / Part II blend in ratio 55/45 against T.

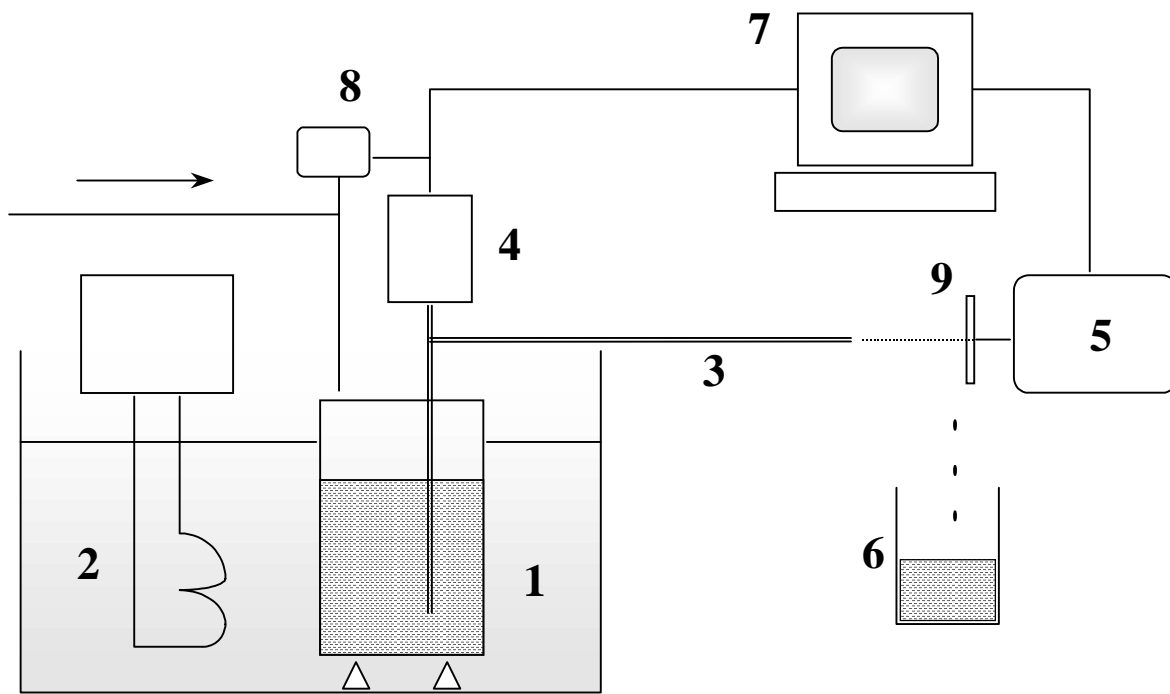


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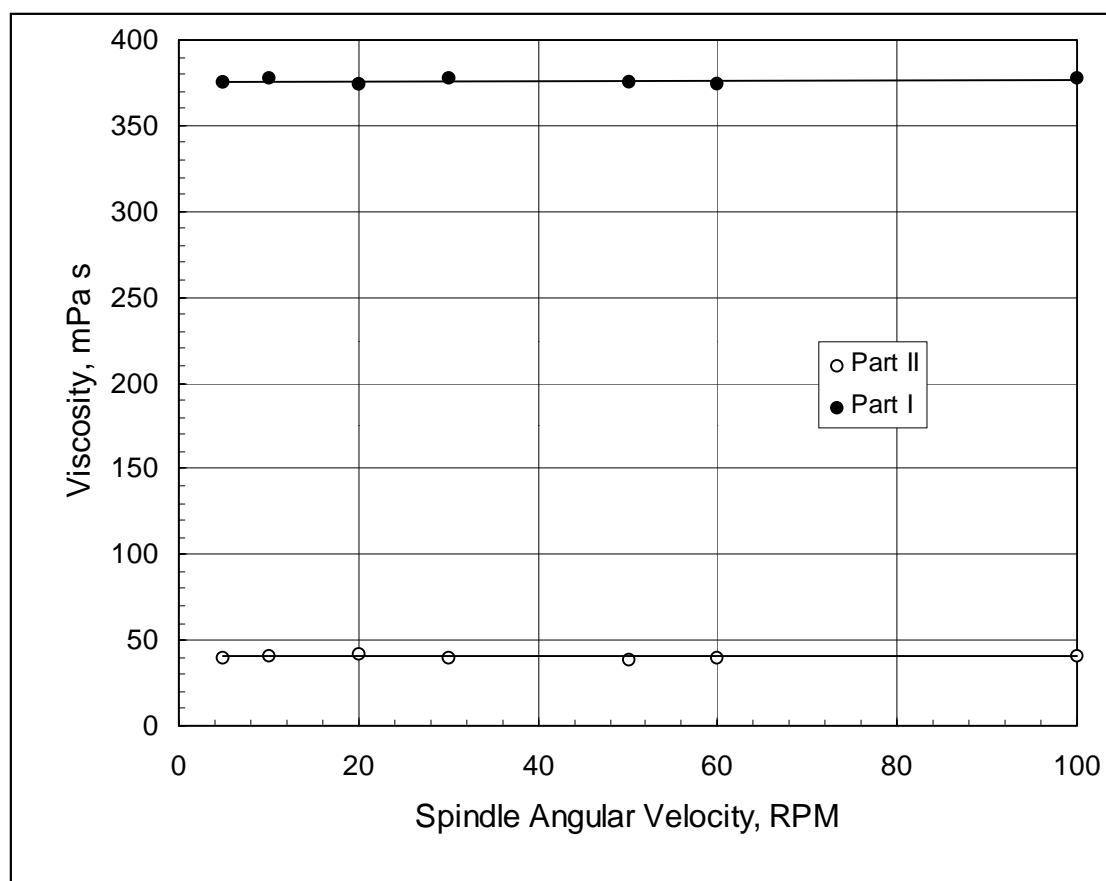


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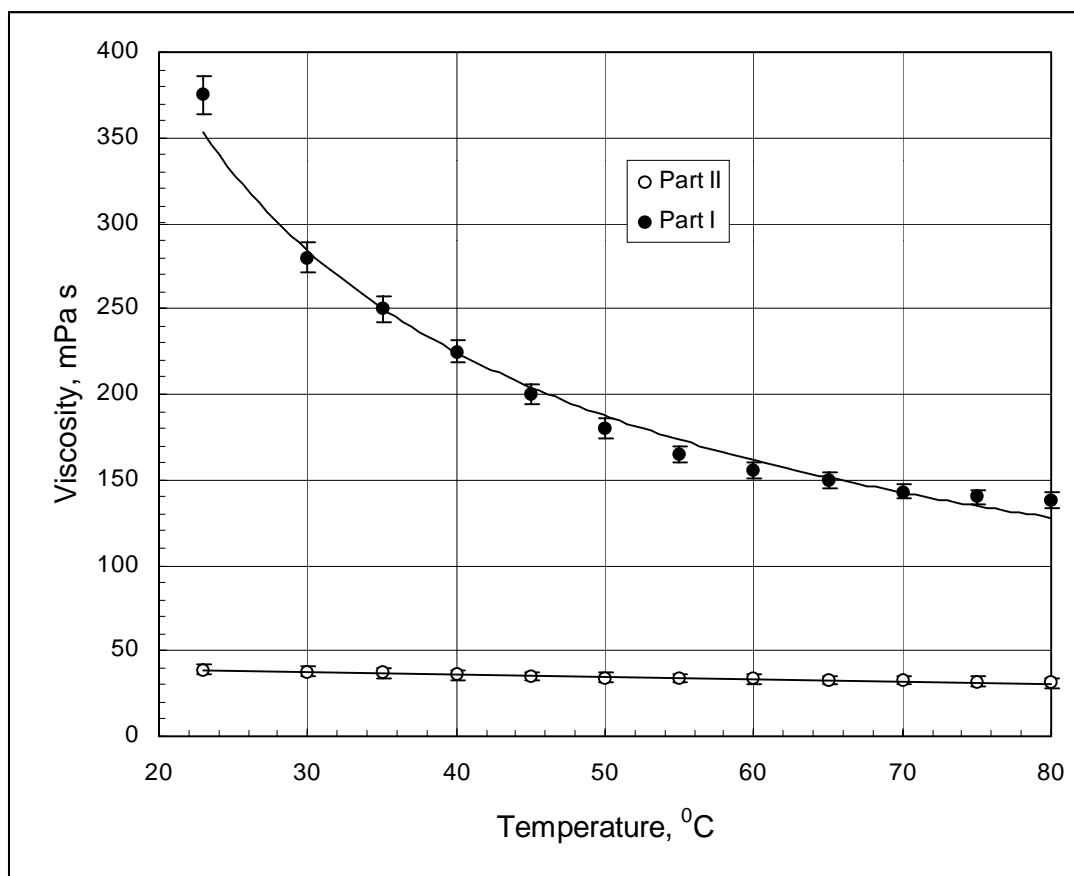


Fig. 3. Variation of viscosity of Part I and Part II against temperature ($\omega = 50$ RPM).

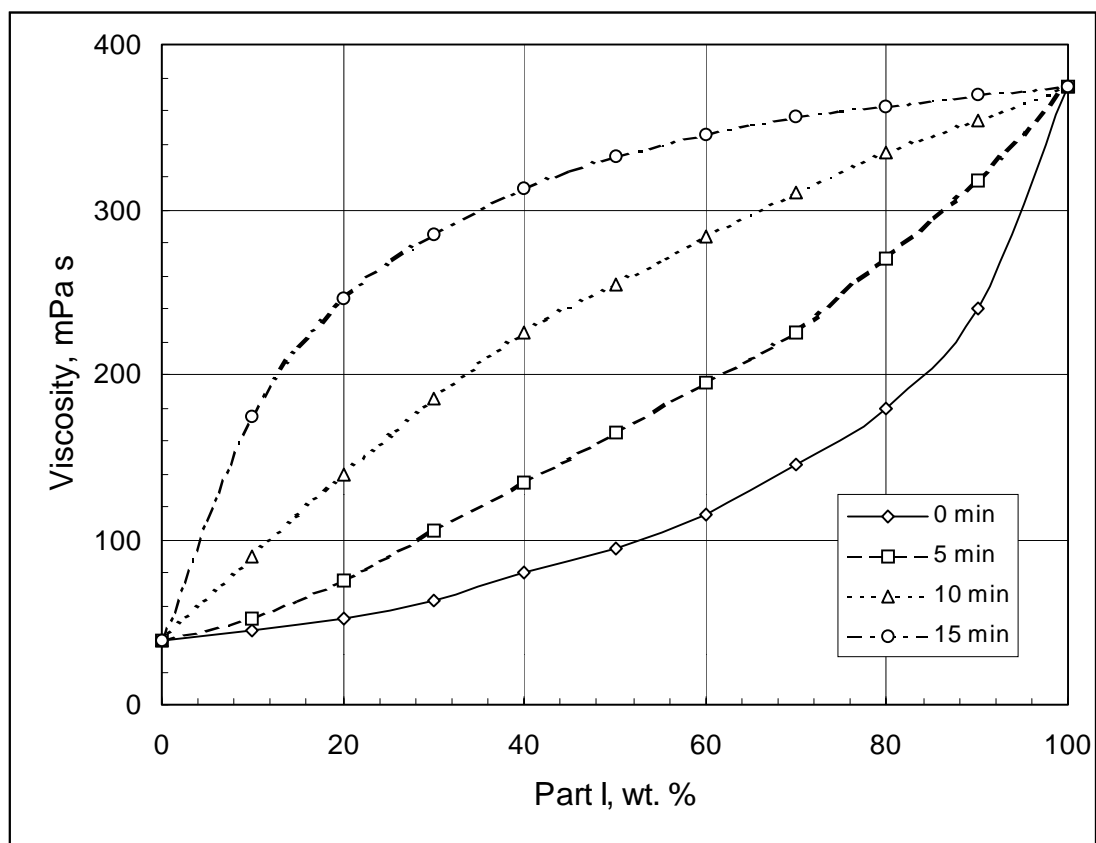


Fig. 4. Variation of viscosity of Part I and Part II blend as a function of Part I composition at different time intervals ($\omega = 50$ RPM, $T = 23^{\circ}$ C).

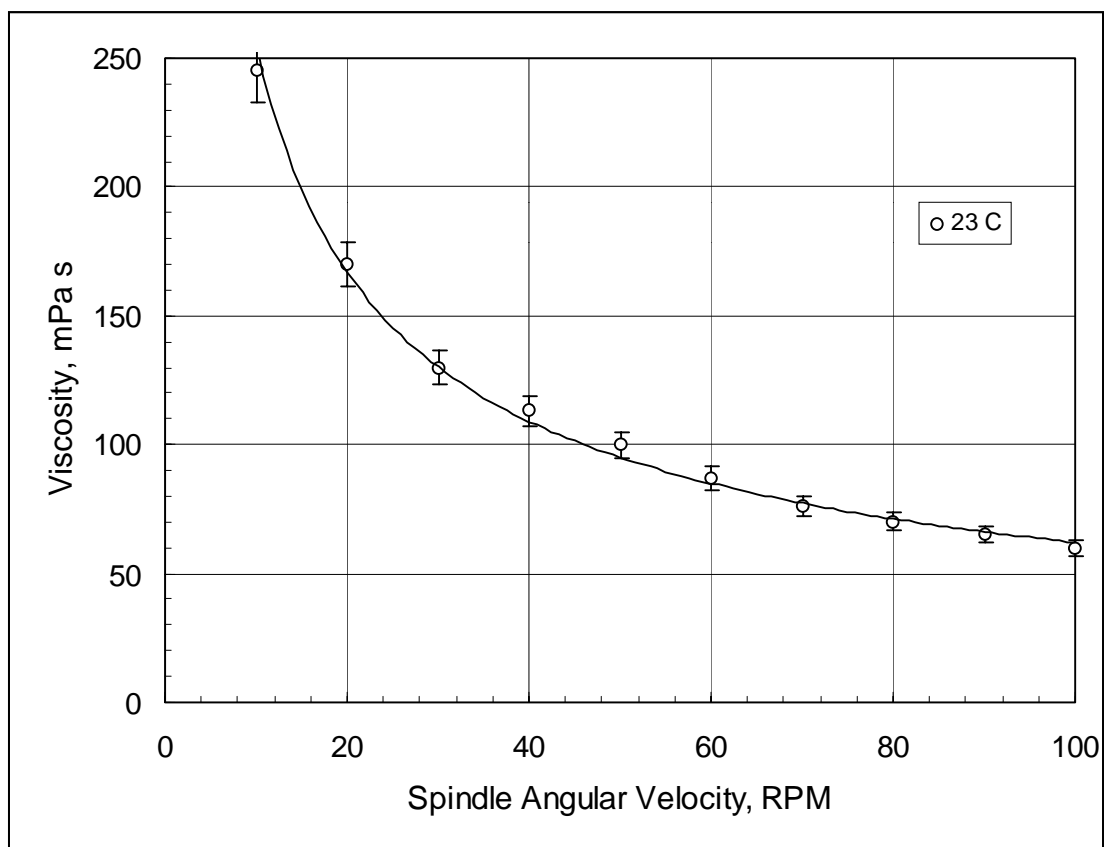


Fig. 5. Variation of Part I / Part II blend (55/45) against spindle angular velocity
($T = 23^{\circ}\text{C}$).

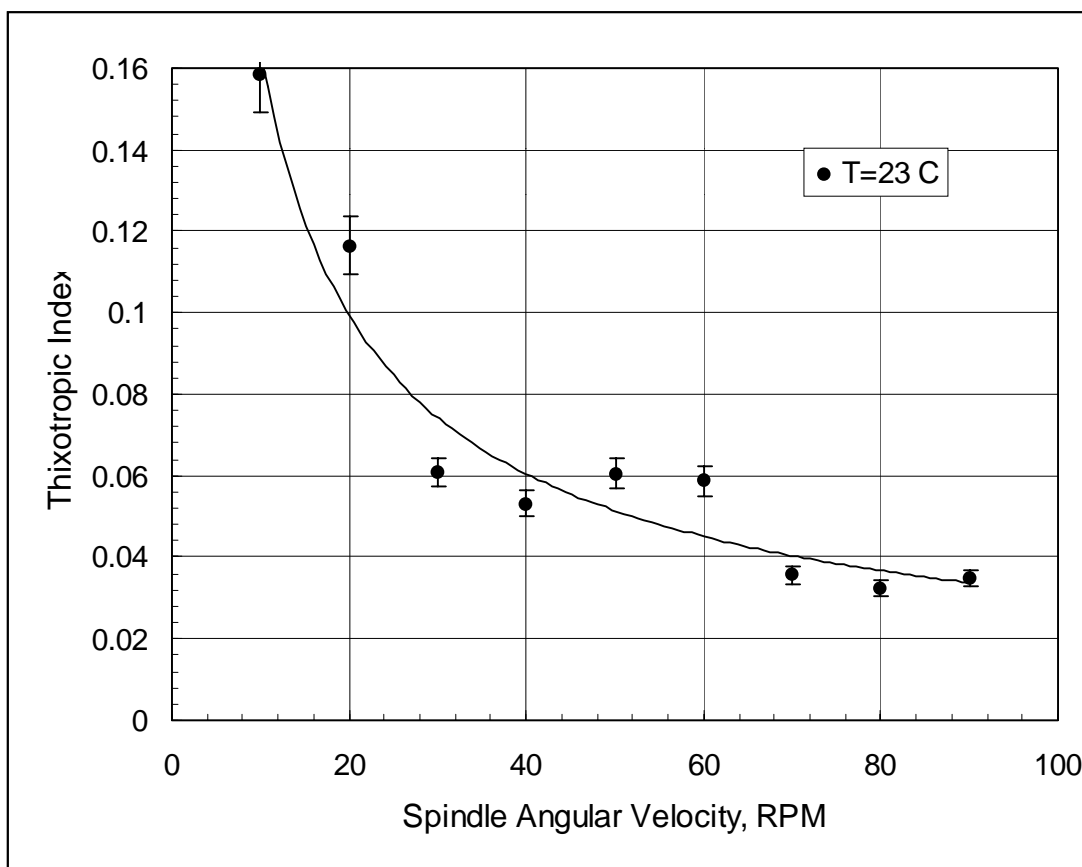


Fig. 6. Variation of Thixotropic index with spindle angular velocity for Part I / Part II

blend in 55/45 ratio at T=23 C.

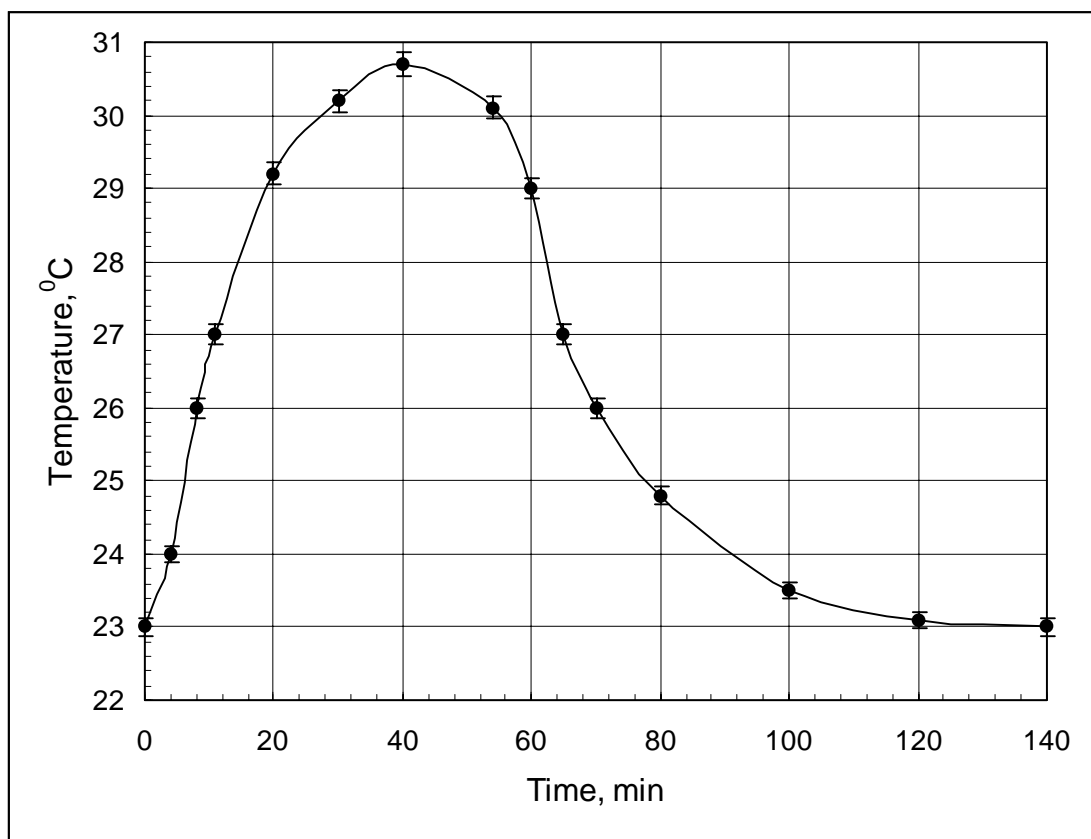


Fig. 7. Variation of temperature yielded at thermoreaction between Part I / Part II in ratio 55/45 against time.

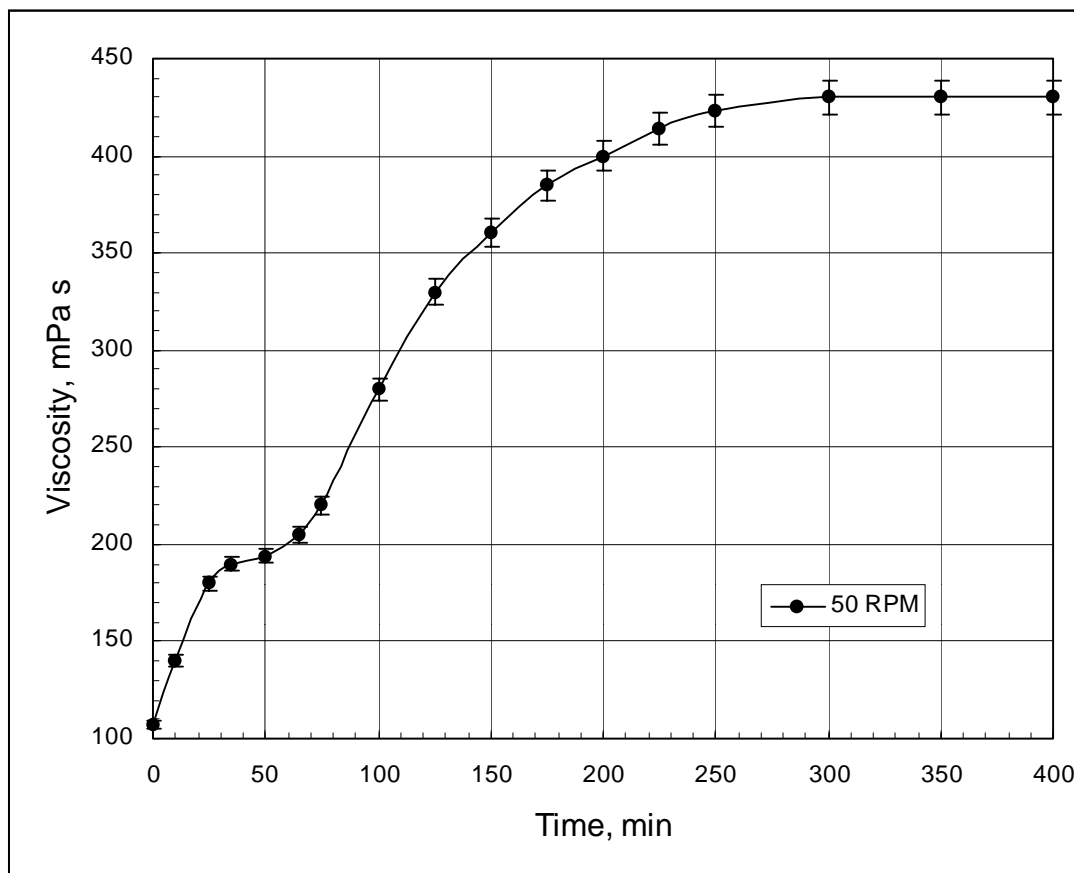


Fig. 8. Variation of viscosity of Part I / Part II blend in ratio 55/45 against time
at $\omega = 50$ RPM.

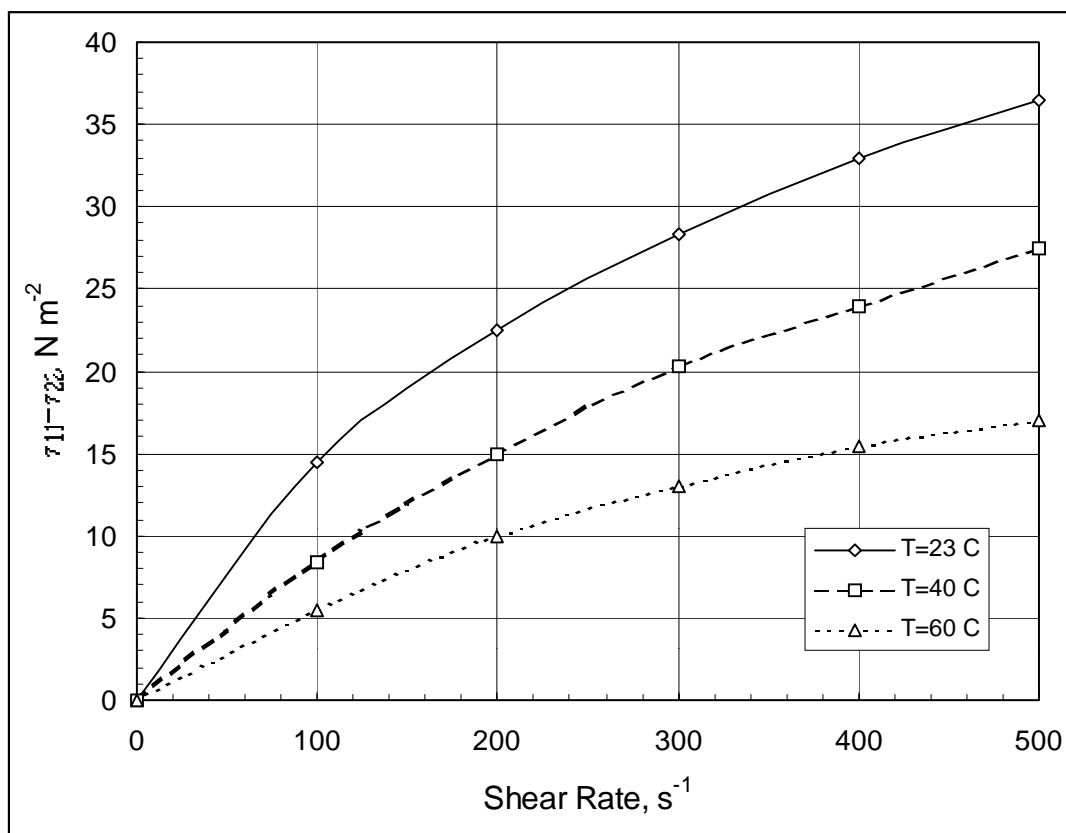


Fig. 9. Variation of first normal stress difference of Part I / Part II blend in ratio 55/45 against shear rate.

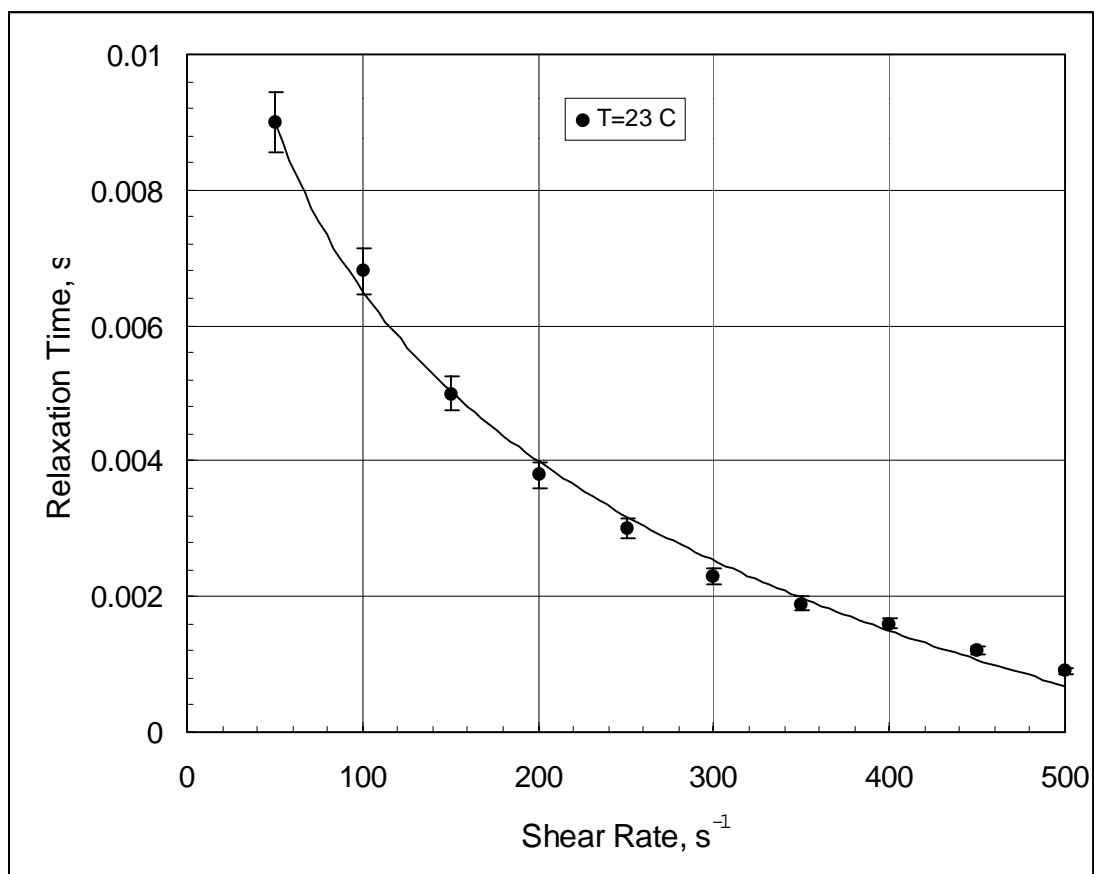


Fig. 10. Variation of relaxation time of Part I / Part II blend in ratio 55/45 against shear rate.

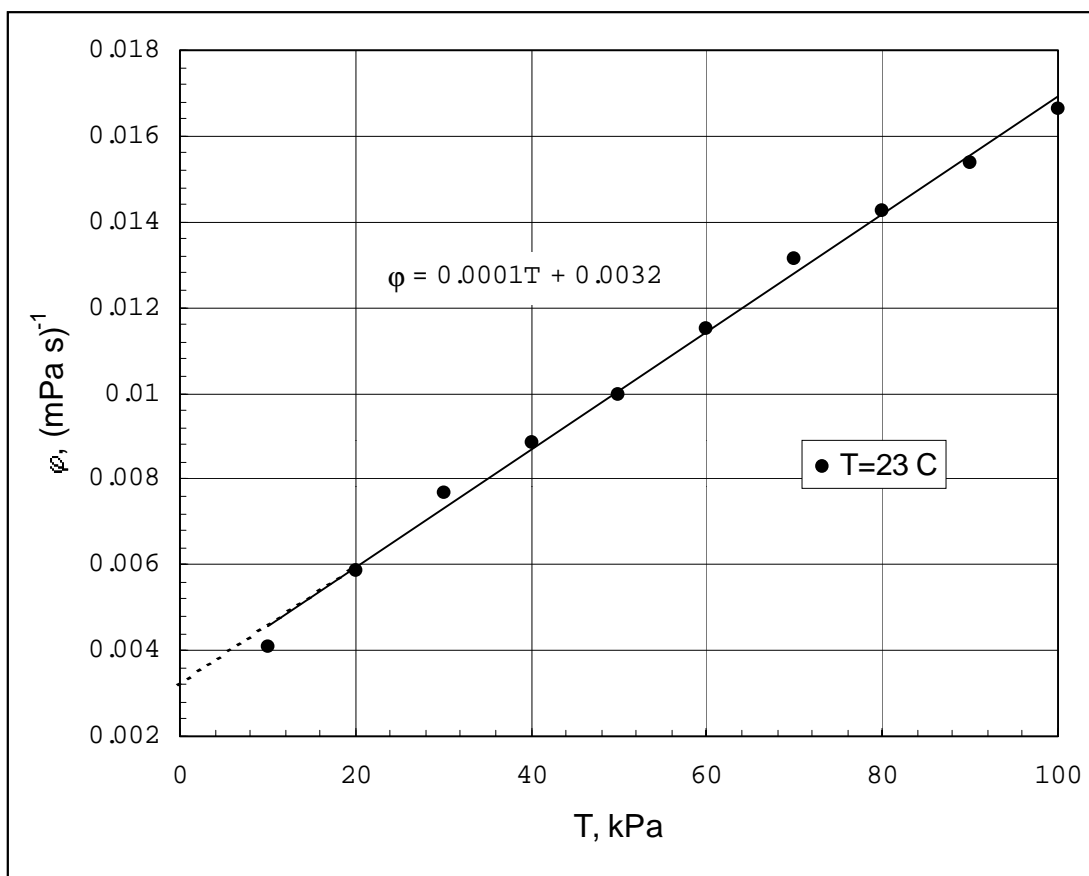


Fig. 11. Variation of fluidity coefficient of Part I / Part II blend in ratio 55/45 against T .